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(66) References cited :
JOURNAL OF APPLIED PHYSICS, vol. 56, no.
6, 15th September 1984, pages 1756-1761,
American Institute of Physics, New York, US;
R. HEZEL et al.: "Silicon oxynitride films pre-
pared by plasma nitridation of silicon and their
application for tunnel metal-insulator-silicon
diodes"
PATENT ABSTRACTS OF JAPAN, vol. 7, no.
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(56) References cited :
EP-A- 0 015 694
US-A- 4 113 515
US-A- 4 277 320
JOURNAL OF THE ELECTROCHEMICAL SOCI-
ETY, vol. 131, no. 3, March 1984, pages
663-666, Manchester, New Hampshire, US; M.
HIRAYAMA et al.: "Plasma anodic nitridation
of silicon in N₂-H₂ system"
Idem
IBM TECHNICAL DISCLOSURE BULLETIN,
vol. 27, no. 4B, September 1984, pages
2560-2563, New York, US; R.S. BENNETT et al.:
"Selective planarization process and struc-
tures"
JAPANESE JOURNAL OF APPLIED PHYSICS,
vol. 20, suppl. 20-1, 1981, pages 33-38, Tokyo,
JP; T. ITO et al.: "(Invited) thermal nitridation
of silicon in advanced LSI processing"
APPLIED PHYSICS LETTERS, vol. 32, no. 5, 1st
March 1978, pages 330-331, American Institute
of Physics, New York, US; T. ITO et al.:
"Thermally grown silicon nitride films for high-
-performance MNS devices"
JOURNAL OF APPLIED PHYSICS, vol. 52, no.
4, April 1981, pages 3076-3079, American Institute
of Physics, New York, US; R. HEZEL et al.:
"Plasma Si nitride - A promising dielectric to
achieve high-quality silicon MIS/L solar
cells"

EP 0 201 380 B1

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Description

BACKGROUND OF THE INVENTION

6 The present invention is directed to a method of forming thin films of silicon nitrides and other nitrogen-containing compositions, such as oxynitrides, directly on a silicon surface, and is further concerned with the application of such films.

10 Thin films of silicon nitride have two significant applications in the field of integrated circuits. Since they exhibit a higher dielectric constant and hence a higher unit capacitance than silicon dioxide layers, their use as capacitor dielectrics in small dimension MOS circuits is preferred. The increased unit capacitance that they exhibit make it possible to fabricate capacitors in smaller areas and hence contributes to a denser circuit, relative to a circuit of similar complexity that employs a silicon dioxide film. In addition, silicon nitride films have greater resistance to radiation, alkali ion and other impurity diffusion.

15 A second application of thin silicon nitride films relates to the electrical isolation of integrated circuits by means of silicon dioxide islands. Typically, these islands are formed by oxidizing selected regions of a silicon substrate. Silicon nitride films are used to protect areas of the substrate where the devices are to be fabricated. In current practice, a thin oxide layer is used between the substrate and a deposited silicon nitride film to prevent the generation of stress-induced faults during oxidation. The presence of this oxide layer permits oxidation to proceed in a lateral, or horizontal, direction as well as in the vertical direction. Oxide encroachment in this lateral direction reduces the area that is subsequently available for fabricating the integrated circuit, and it is therefore preferable to minimize such. Accordingly, attempts have been made to form the thin nitride layer directly on the silicon substrate.

20 In the past, several different techniques have been employed to form a silicon nitride layer directly on the surface of a silicon substrate. One such technique is the thermal nitridation of silicon, which is carried out using ammonia or nitrogen gases at temperatures in the neighborhood of 1000°C or greater. This approach is disadvantageous in that it requires treatment at high temperatures for extended periods of time and is limited in the types of materials which can be present on or in the substrate. It is particularly unsuitable for use in the fabrication of VLSI devices, since the susceptibility of dopants to diffusion at high temperatures presents problems with the small geometries that are involved. In addition, the resultant films contain a significant amount of oxygen, which hampers their effectiveness in resisting oxidation.

25 A variation of this technique involves plasma-assisted thermal nitridation with the use of inductively coupled reactors. This technique is disclosed, for example, in U.S. Patent Nos. 4,277,320 and 4,298,629. A coil disposed around the reaction chamber generates an electromagnetic field that inductively heats the wafer to be coated and excites the gas within the chamber to create a plasma. Such reactors have proven to be difficult to construct on a production-scale level, and are therefore not in widespread use. Furthermore, they operate at relatively high temperatures (close to 1000°C) that are produced by the inductive field, and hence have high power requirements.

30 Another technique for forming thin nitride films uses high energy ion implantation. This technique is generally not desirable from a commercial standpoint, since its throughput is limited by the relatively small ion beam that is employed. In addition, high current implantation systems are complex and expensive.

35 Low energy ion bombardment is a third technique that has been used to prepare nitride-like films on silicon. Limitations associated with this technique include the fact that processing can only be carried out on a single wafer at a time because of the beam size generated by presently available low energy ion bombardment sources, and the contamination of the resulting layer with materials that are used to fabricate the ion gun source.

40 A fourth technique for forming silicon nitride films is low pressure chemical vapor deposition (LPCVD). Thickness control of thin films is difficult with this process, and hence the films tend to be relatively thick, in the neighborhood of 300 angstroms or more. As a result, they are not suitable for use in trench isolation when in direct contact with silicon because they can produce stress at the corners of the trench, which leads to defects in adjacent regions of the silicon substrate.

45 Document JP-A-83242-1983 discloses a method of forming a nitride on a silicon substrate by directly reacting nitrogen containing gas with the surface of the silicon substrate. In a reaction chamber, two parallel flat electrodes are disposed facing one another. One of the electrodes carries the wafer and is connected to ground. The other electrode is supplied with r.f. power in the MHz range. Further, the wafer carrying electrode and the wafer itself are heated by means of an induction coil beneath the electrode and fed with r.f. power in the KHz range. The wafer is negatively DC biased. Nitridation takes place at temperatures of about 800°C. Nitride film thicknesses vary between 7 and 15 nm (70 and 150 Angstroms) depending upon the nitridation time of 20 to 90 minutes.

50 Document J.Appl.Phys. 52(4), 3076 (1981), R. Hezel et al. "Plasma Si nitride - A promising dielectric to

achieve high-quality silicon MIS/IL solar cells" discloses a so-called low temperature plasma-enhanced chemical vapor deposition of silicon nitride. Low temperature, in the context of this document, designates a substrate temperature of 220°C.

5 The present invention as it is defined by patent claim 1 distinguishes over the former document in that the electrodes have substantially different sizes and that the substrate is cooled such that a temperature of 200°C is not exceeded; preferably, the process is carried out at room temperature. It has been found that under these conditions, the process is self-limiting, i.e. the silicon nitride film thickness ultimately obtained will not increase beyond a certain value upon continued treatment, said value depending upon the applied power.

10 **OBJECTS AND BRIEF STATEMENT OF THE INVENTION**

Accordingly, it is an object of the present invention to provide a novel means for economically converting the surfaces of silicon and similar materials into nitride-like layers at relatively low temperatures, i.e. at or near room temperature. In particular, it is an object of the invention to provide a novel method for forming silicon 15 nitride layers, which method does not require an ion gun source and minimizes the energy of ions incident on metallic surfaces, to thereby keep the sputtering and subsequent redeposition of potential contaminants onto the wafer surface low. It is a further object of the invention to provide a novel method of the foregoing type which provides effective control over the thickness of the nitride layer that is formed.

It is a further object of the invention to provide novel applications for thin nitride films.

20 In accordance with the present invention, these objects are achieved by carrying out a surface reaction on a substrate layer in a vacuum chamber that contains an electrode which is capacitively coupled to an rf generator. A second electrode within the chamber, or a metal wall of the chamber itself, is connected to ground. The silicon wafers to be treated are placed on one of the electrodes to be in electrical and physical contact therewith, and a reagent gas that contains nitrogen is introduced into the chamber. An rf voltage is then applied 25 between the electrodes to create a plasma, causing ions thereof to be accelerated into the silicon substrate. The nitrogen ions that are created as a result of the application of the rf power can be directed at the surface of a number of wafers simultaneously, thereby providing improved throughput over the prior art techniques. In addition, the growth process is self-limiting, thereby providing effective control over the thickness of the silicon nitride layer, enabling films that are in the range of 50-100 angstroms thick to be consistently produced.

30 The thin nitride films that are formed by such a method have a variety of useful applications. Because of their high degree of integrity and high nitrogen-to-oxygen ratio, they are well suited for preventing oxidation during device isolation. Furthermore, the controllability of the thickness of the films readily facilitates the fabrication of capacitors having high unit capacitance. For greater reliability and to reduce leakage currents, the films can be annealed in an oxygen atmosphere when they are to be incorporated in capacitor structures. In 35 addition, the electrical properties of such a film, coupled with its immunity to impurity diffusion and radiation, contribute to its successful application as a gate dielectric for MOSFET devices.

Further features of the invention are described in detail hereinafter with reference to preferred embodiments thereof illustrated in the accompanying drawings.

40 **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a schematic representation of a chamber of the type that can be used to implement the process of the present invention;

45 Figures 2 and 3 are cross-sectional views of a silicon wafer during steps of a LOCOS isolation process;

Figure 4 is a cross-sectional view of a trench isolation structure;

Figure 5 is a cross-sectional view of a trench capacitor structure; and

Figure 6 is a cross-sectional view of a MOSFET device incorporating a thin nitride film in the gate dielectric.

50 **DESCRIPTION OF PREFERRED EMBODIMENTS**

The method of the present invention for forming a thin film of nitride directly on the surface of a silicon substrate can be carried out in an apparatus of the type illustrated in Figure 1. For example, this apparatus could be a chamber of the type that is typically used for plasma etching. This apparatus basically comprises a sealed metal-walled chamber 10 having a cathode 12 that is electrically insulated from the remainder of the chamber walls, for example by means of a glass insulating ring 14. One wall of the chamber is provided with a loading port 16 to enable silicon wafers to be placed on the cathode 12 and removed therefrom. A vacuum source, such as a turbo-molecular pump 18, is in communication with the chamber to thereby evacuate the same. In addition, the chamber is provided with a gas introduction tube 20 that is connected to a source 22 of

a suitable nitrogen-containing gas through a pressure regulator 24. If appropriate, suitable moisture and oxygen removing cannisters (not shown) can be connected to the tube 20 to improve the purity of the gas that is introduced into the chamber.

The cathode 12 is coupled to an rf generator 26 by means of an in-line capacitor 28, and the metallic walls of the chamber 10 are connected to ground to form an anode. The cathode and the anode thus form a pair of spaced plate electrodes. The generator 26 provides an a.c. current to the cathode at an rf frequency, and the in-line capacitor 28 maintains a d.c. bias on the electrode. Preferably, the area of the anode is much greater than that of the cathode, so that a relatively high self bias, in the range of 300 to 1100 volts, is created at the cathode.

In operation, after the silicon wafers are placed on the cathode 12, and the loading port 16 is closed to seal the chamber, it is evacuated by means of the pump 18 to a low base pressure so as to minimize potentially contaminating residual gases. This base pressure is preferably about 10^{-6} Torr. To effect nitridation, gas from the source 22 is introduced continuously into the evacuated chamber through the tube 20 to maintain the pressure within the chamber at about 10^{-2} Torr. This gas could be pure nitrogen, ammonia or a nitrogen-hydrogen mixture, for example.

The gas within the chamber is activated by applying the power from the rf generator 26 to the cathode. This power can be in the range of about 25 to about 500 watts, and has a frequency of 10 KHz to 300 MHz. As a result of the rf power, a plasma of energized ions of the gas is created. These ions are accelerated into the silicon substrate that is in electrical and physical contact with the cathode, to form a silicon nitride layer.

In order to minimize heating of the silicon wafers as well as prevent cracking of the cathode due to overheating, the cathode can be cooled by any suitable arrangement, such as a water distribution system 30. To inhibit the sputtering of oxygen-containing materials from the glass insulating ring 14 that supports the electrode, a dark space shield 32 can be provided around the electrode. This shield can be made of a suitable conductive material such as aluminum or stainless steel, and can be grounded.

A capacitively coupled rf system such as that illustrated in Figure 1 is capable of creating nitrogen-containing ions of sufficient energy and flux to the surface of the wafer supported on the cathode 12. In contrast to prior systems that employ thermal energy to induce a surface reaction, the system of the present invention utilizes electrically excited nitrogen-containing ions and accelerates them into the silicon surface to promote the chemical reaction. Since the ions can be directed at a relatively large area, a number of wafers can be processed simultaneously, thus making the method of the present invention an economic one for converting the surfaces of silicon into nitride-like layers. In addition, the process is carried out at a relatively low temperature e.g., less than 200°C. (and preferably at room temperature) and does not require an ion gun source.

Furthermore, the process provides inherent control over the thickness of the film that is formed, enabling relatively thin films that are less than 200 angstroms thick, and preferably about 50-100 angstroms thick, to be consistently produced. In particular, the process is self-limiting in that the net growth rate of the nitride film is inversely related to the film's thickness for a given power density. When the film obtains a thickness where its growth rate is equal to the constant rate at which ions sputter off its surface, the process reaches a steady state and no further net growth occurs. For example, for a power density of 0.4 W/cm² of the wafer, the thickness of the film only increases by 5% as the process time is increased from 2 minutes to 45 minutes. By adjusting the power density, films of different desired thicknesses can be obtained.

The control that is afforded by the process described above and the quality of the resulting film facilitate its use in a variety of applications. Through appropriate selection of the density of the applied power (i.e. watts per cm² of the wafer), the atomic nitrogen to nitrogen-plus-oxygen ratio ([N]/[N+O]) of the film can be regulated for a desired application. For example, if the nitride film is to be used to prevent oxidation of selected areas of the wafer during field oxidation, [N]/[N+O] should preferably be at least 90%. When the plasma is formed from N₂, and using an anode:cathode ratio of about 20, powered by a 13.56 MHz rf generator, the [N]/[N+O] ratio can be varied in a range from about 82% (power density = 0.4 W/cm²) to about 98% (power density = 3.2 W/cm²) for 5 minutes. If NH₃ is used to form the plasma, the [N]/[N+O] ratio goes from about 78% to about 96% for the same respective power density settings and time.

Referring to Figures 2 and 3, one application of the nitride film is illustrated. After a nitride film 36 has been deposited on a silicon substrate 38 in accordance with the method described above, a portion of the film is etched away to define a field region. The portions of the film which remain define the active areas where devices are to be formed. The field regions 40 are oxidized as shown in Figure 3b to provide isolation. The nitride film 36 protects the underlying substrate from oxidation. When the [N]/[N+O] ratio of the film 36 is at least 90%, it has been found that the film will resist more than 4500 angstroms of oxidation.

Subsequent to the formation of the nitride layer, it can be annealed if desired. Such annealing can be carried out by heating the wafer to a temperature between 900 and 1100°C. In order to prevent oxidation of the film, a chamber in which the annealing is carried out can be filled with a non-oxidizing gas such as nitrogen,

hydrogen, or another inert gas. Alternatively, the chamber can be evacuated to achieve the same effect.

Furthermore, the process is not limited to the formation of thin nitride films on planar surfaces. Of particular interest in this context is the formation of the film within trenches. It has been found that high quality thin films can be formed along the side and bottom walls of trench structures in a silicon substrate. Thus, the nitride film can be used as an integral part of the insulating material that fills the trenches for dielectric device isolation.

Referring to Figure 4, a trench 42 is cut into the surface of a silicon wafer to define a boundary between active areas. If desired, the trench could completely surround an active area. The side and bottom walls of the trench are lined with a thin layer 44 of nitride. Preferably, this layer is only 50-70 angstroms thick. The remainder of the trench is then filled with a suitable material 46, such as silicon dioxide or undoped polysilicon. The nitride liner 44 on the walls of the trench acts as a suitable barrier to the diffusion of the material into the silicon substrate.

Advantage can also be taken of the relatively high dielectric permittivity of the film formed according to the above-described process. In particular, silicon nitride has a higher dielectric constant than silicon dioxide. Furthermore, as the thickness of the film is reduced its capacitance increases, so that the relatively thin films that can be obtained with the present invention offer high unit capacitance. To further increase the capacitive applications of nitride films formed according to the process of the invention, they can be annealed in an oxidizing atmosphere to reduce their leakage current.

For example, when used in a dynamic random access memory (DRAM), an integrated capacitor should have high unit capacitance, e.g., at least 5 fF/micron², so as to be capable of storing a sufficiently large charge packet that provides immunity to noise. In addition, the capacitor should exhibit low leakage current, e.g. no greater than 10⁻⁶ A/cm² at 2.5 V, so as to afford a refresh cycle time of sufficient duration. The following table illustrates how the properties of a capacitor formed according to the present invention can be improved by annealing it in an oxygen atmosphere. The examples given in the table are with respect to a nitride film formed on a silicon wafer exposed to a plasma created from N₂ gas using an anode:cathode ratio of about 20, powered by a 13.56 MHz rf generator at a power density of 0.4 W/cm² for five minutes, in accordance with the above-described process. The oxygen anneal is carried out at 1000°C.

30	Anneal Time (min)	Capacitance (fF/micron ²)	Leakage Current at 2.5 V (A/cm ²)
	0	*	> 10 ⁻⁵
	30	8.8	6 x 10 ⁻⁶
	90	7.7	1.2 x 10 ⁻⁷

35

* Not capable of precise measurement due to high leakage current.

40

As can be seen, the unit capacitance of the film undergoes a slight decrease when annealed, most likely due to its increased thickness and oxygen content as it undergoes oxidation. However, even with an anneal for 90 minutes, the unit capacitance still remains well above the minimum noted previously for DRAM applications, whereas the leakage current is reduced by two orders of magnitude over a film which has not been annealed.

The annealing temperature and time can be shortened, for example by utilizing steam at 900°C for 10-15 minutes. As another alternative, it is possible to employ a rapid thermal anneal (RTA) in which high temperatures are applied to the wafer for very short periods of time, e.g., tens of seconds. It is believed that results which are equivalent to or better than those depicted above can be obtained with these alternative annealing processes.

Due to the ability of the inventive process to produce high-quality nitride films within trenches, it becomes possible to fabricate trench capacitor structures. Such a structure is illustrated in Figure 5. The capacitor basically comprises a thin nitride film 48 formed along the upper surface and within a trench formed in an appropriately doped layer 50 of silicon or polysilicon. The layer 50 functions as one electrode of the capacitor, and a second electrode 52 is formed by depositing a metal or doped polysilicon over the nitride layer 48. If the trench has a width W and a depth D, its capacitance would be (1 + 4D/W) times greater than that of a capacitor formed on top of layer 50 and occupying the same amount of surface area.

Another particularly useful application for nitride films formed according to the process of the present in-

vention is as a gate dielectric for MOSFET devices. In the past, attempts at constructing a MOSFET using a thin oxide film in the gate region and a doped polysilicon for the gate conductor have met with several limitations. One of these limitations has been with respect to the impurity that is used to dope the polysilicon. Boron would be a desirable dopant for the polysilicon layer to produce an enhancement type MOSFET. However, the diffusion coefficient for boron is enhanced in the presence of hydrogen during the deposition of polysilicon. Consequently, it tends to break through the oxide layer and dope the underlying channel region. Phosphorous dopant would be another possibility but it suffers from the fact that it would create a depletion type of n-channel MOSFET.

However, by using a nitride film as the gate dielectric, the tendency of boron to diffuse into the channel region is resisted. Furthermore, even though the interface state density of the nitride film is higher than that of silicon dioxide layers, the nitride's contribution to the threshold voltage of the device is minimal, due to its small thickness and high permittivity. Therefore, it is possible to produce enhancement type MOSFETs of higher reliability and integrity using a combination of the above-mentioned features.

Such a device is illustrated in Figure 6. The device comprises a channel region 54 of silicon that is doped to one conductivity, e.g. n-type. Source and drain regions 56 of opposite conductivity are located on opposite sides of the channel region. A thin film of silicon nitride 58 is grown over the channel region to provide the gate dielectric. A silicon dioxide layer 60 covers the remaining portion of the surface of the substrate, and suitable contact holes 62 are provided for the source and drain electrodes. A thin layer of silicon dioxide 64 can also be disposed over the nitride film. In fact, the interface between the nitride layer 58 and the silicon dioxide layer 64 may not be well-defined, but rather comprise a blend from primarily nitride to primarily oxide over a distance of 5-20 angstroms. A polysilicon layer 66 that is doped with boron is deposited over the thin gate dielectric films 58 and 64 to form the gate electrode.

In summary, the nitride films that are produced according to the process of the present invention have at least two significant areas of application, as barriers for isolation and during oxidation, and as elements of electrical devices such as capacitors and MOSFETs. In the former area of application, it is desirable that the film have a high purity, i.e., $[N]/[N+O]$ is high. Accordingly, the process should be carried out at relatively high power density levels, e.g., 1.6-3.2 W/cm², and at relatively low pressures. For electrical applications, where the film is preferably annealed in oxygen, its purity is not so much a factor as its electrical characteristics. Accordingly, the process can be carried out with lower power densities, for example in the range of 0.4-2.0 W/cm². Further in this regard, films made with N_2 as the source appear to be best suited for use as gate dielectrics, whereas those made with NH_3 are preferred for use in capacitors since they exhibit higher unit capacitance for a given leakage current.

35 Claims

1. A method of preparing a thin film of silicon nitride or other nitrogen-containing composition on a silicon substrate, in a capacitively coupled plasma deposition chamber with parallel electrodes comprising the steps of:
 - 40 placing one surface of silicon substrate in contact with a first of a pair of plate electrodes, said first electrode being spaced away and opposite from a second plate electrode of said pair of electrodes which faces the opposite surface of said substrate and has an area greater than said first of said pair of electrodes;
 - 45 evacuating a chamber in which said electrodes and the substrate are located;
 - introducing a nitrogen-containing reagent gas free of silicon compounds into the space between said pair of electrodes; and
 - 50 applying an a.c. voltage having a frequency of about 10 KHz or greater between said electrodes to thereby ionize and activate the reagent gas and accelerate ions thereof into the substrate while cooling said first of said pair of electrodes to inhibit heating of said substrate wherein the temperature of said substrate is less than 200°C.
2. The method of claim 1 wherein said reagent gas comprises one of pure nitrogen, ammonia and a nitrogen-hydrogen mixture.
3. The method of claim 1 further including the step of annealing the thin film of nitride formed on said substrate.
4. The method of claim 3 wherein said annealing step is carried out in the presence of a non-oxidizing gas.

5. The method of claim 1 wherein the area of the other electrode of said pair of electrodes is at least twice as great as the area of said one electrode.
6. The method of one of the preceding claims for isolating active regions from one another in an integrated circuit, comprising the steps of:
 - removing selected portions of said film so that the remaining portions of the film correspond to areas in which active devices are to be formed in the wafer; and
 - oxidizing the areas on said surface of the wafer that are not covered by the remaining portions of the nitride film.
10. The method of claim 6 wherein said a.c. voltage signal has a power density in the range of about 1.6 to about 3.2 W/cm² of the substrate.
15. The method of claim 6 wherein said nitride film has a thickness no greater than 20 nm (200 angstroms).
19. The method of claim 8 wherein said film has a thickness in the range of about 5 to about 10 nm (50 to about 100 angstroms).
20. The method of claim 6 wherein the ratio of nitrogen to nitrogen-plus-oxygen in said film is at least 90%.
21. The method of claim 6 wherein the pressure of said plasma is about 10⁻² Torr.
25. The method of claim 8 wherein said opposite surface of the substrate has a trench in it, and said nitride film remains in the trench after said selective removing step.
29. The method of one of claims 1 to 5 for dielectrically isolating active regions from one another in an integrated circuit, comprising the steps of:
 - forming a trench in the exposed surface of said substrate to define a boundary of at least one area in which an active device is to be located; and after said nitride film is formed on said surface of the substrate and along the walls of said trench:
 - filling the remainder of said trench with an insulating material.
35. The method of claim 13 wherein said film has a thickness of about 5 to about 7 nm (50 to about 70 angstroms).
39. The method of claim 13 wherein said a.c. voltage signal has a power density in the range of about 1.6 to about 3.2 W/cm² on the substrate.
40. The method of claim 13 wherein the ratio of nitrogen to nitrogen-plus-oxygen in said film is at least 90%.
41. The method of claims 1, 2, and 3 wherein said a.c. voltage signal has a power density of about 0.4 to about 2.0 W/cm² of the substrate.
45. The method of claim 17 further including the step of depositing an electrode on the surface of said nitride film that is opposite the silicon to thereby form a capacitor.
49. The method of claim 18 wherein said nitride film comprises the gate dielectric for a MOSFET, and further including the step of depositing a doped polysilicon on said film to form the gate electrode of the MOSFET.
50. The method of claim 19 wherein said polysilicon is doped with boron.
54. The method of claim 19 further including the step of forming a thin layer of oxide between said nitride film and said polysilicon gate electrode.
55. The method of claim 3 wherein said annealing is carried out in the presence of oxygen.

Patentansprüche

1. Ein Verfahren zum Bilden einer dünnen Schicht von Siliciumnitrid oder einer anderen Stickstoff enthaltenden Zusammensetzung auf einem Siliciumsubstrat in einer kapazitiv gekoppelten Plasmaauflagkammer mit parallelen Elektroden, umfassend die Schritte:
 - 5 Plassieren einer Oberfläche des Siliciumsubstrats in Kontakt mit einer ersten eines Paares von Plattenelektroden, welche erste Elektrode von einer zweiten Plattenelektrode des Paares von Elektroden abstandet ist und dieser gegenüberliegt, welche der entgegengesetzten Oberfläche des Substrats zu gewandt ist und eine Fläche aufweist, die größer ist als die erste des Paares von Elektroden;
 - 10 Evakuieren einer Kammer, in der sich die Elektroden und das Substrat befinden;
 - 15 Einspeisen eines Stickstoff enthaltenden Reagenzgases, das frei von Siliciumverbindungen ist, in den Raum zwischen dem Paar von Elektroden; und
- 20 Anlegen einer Wechselspannung mit einer Frequenz von etwa 10 KHz oder größer zwischen den Elektroden, um dadurch das Reagenzgas zu ionisieren und aktivieren und Ionen desselben in das Substrat zu beschleunigen, während die erste des Paares von Elektroden gekühlt wird, um das Aufheizen des Substrats zu unterbinden, wobei die Temperatur des Substrats bei weniger als 200°C liegt.
- 25 2. Das Verfahren nach Anspruch 1, bei dem das Reagenzgas eines von reinem Stickstoff, Ammonium und einem Stickstoff-Wasserstoff-Gemisch umfaßt.
- 30 3. Das Verfahren nach Anspruch 1, ferner umfassend den Schritt des Anlassens der dünnen Schicht aus Nitrid, die auf dem Substrat gebildet worden ist.
- 35 4. Das Verfahren nach Anspruch 3, bei dem der Anlaßschritt in Gegenwart eines nichtoxidierenden Gases ausgeführt wird.
- 5 Das Verfahren nach Anspruch 1, bei dem die Fläche der anderen Elektrode des Paares von Elektroden mindestens zweimal so groß ist wie die Fläche der einen Elektrode.
- 30 6. Das Verfahren nach einem der vorangehenden Ansprüche für das Isolieren von aktiven Bereichen von einander in einem integrierten Schaltkreis, umfassend die Schritte:
 - 35 Abtragen ausgewählter Abschnitte der Schicht so, daß die verbleibenden Abschnitte der Schicht den Flächen entsprechen, in welchen aktive Komponenten in dem Wafer zu bilden sind; und
 - 40 Oxidieren der Bereiche auf der Oberfläche des Wafers, die nicht von den verbleibenden Abschnitten der Nitridschicht abgedeckt sind.
- 45 7. Das Verfahren nach Anspruch 6, bei dem das Wechselspannungssignal eine Leistungsdichte im Bereich von etwa 1,6 bis etwa 3,2 W/cm² des Substrats hat.
- 50 8. Das Verfahren nach Anspruch 6, bei dem die Nitridschicht eine Dicke von nicht mehr als 20 nm (200 Å) hat.
9. Das Verfahren nach Anspruch 8, bei dem die Schicht eine Dicke im Bereich von etwa 5 bis etwa 10 nm (50 - etwa 100 Å) hat.
- 45 10. Das Verfahren nach Anspruch 6, bei dem das Verhältnis von Stickstoff zu Stickstoff-plus-Sauerstoff in der Schicht mindestens 90% beträgt.
11. Das Verfahren nach Anspruch 6, bei dem der Druck des Plasmas etwa 10⁻² Torr beträgt.
- 50 12. Das Verfahren nach Anspruch 6, bei dem die gegenüberliegende Oberfläche des Substrats einen Graben aufweist und die Nitridschicht in dem Graben nach dem selektiven Abtragschritt verbleibt.
- 55 13. Das Verfahren nach einem der Ansprüche 1 bis 5 für die dielektrische Isolation aktiver Bereiche voneinander in einem integrierten Schaltkreis, umfassend die Schritte:
 - 60 Bilden eines Grabens in der exponierten Oberfläche des Substrats zum Definieren einer Grenze mindestens eines Bereichs, in welchem eine aktive Komponente zu positionieren ist; und, nachdem die Nitridschicht auf der Oberfläche des Substrats und längs der Wandungen des Grabens gebildet worden

ist,

Füllen des Restes des Grabens mit einem isolierenden Material.

- 6 14. Das Verfahren nach Anspruch 13, bei dem die Schicht eine Dicke von etwa 5 bis etwa 7 nm (50 bis etwa 70 Å) hat.
- 10 15. Das Verfahren nach Anspruch 13, bei dem das Wechselspannungssignal eine Leistungsdichte im Bereich von etwa 1,6 bis etwa 3,2 W/cm² auf dem Substrat hat.
- 15 16. Das Verfahren nach Anspruch 13, bei dem das Verhältnis von Stickstoff zu Stickstoff-plus-Sauerstoff in der Schicht mindestens 90% beträgt.
- 20 17. Das Verfahren nach Ansprüchen 1, 2 und 3, bei dem das Wechselspannungssignal eine Leistungsdichte von etwa 0,4 bis etwa 2,0 W/cm² des Sustrats hat.
- 25 18. Das Verfahren nach Anspruch 17, ferner umfassend den Schritt des Aufbringens einer Elektrode auf der Oberfläche der Nitridschicht, die dem Silicium abgekehrt ist, um dadurch einen Kondensator zu bilden.
- 30 19. Das Verfahren nach Anspruch 18, bei dem die Nitridschicht das Gate-Dielektrikum für einen MOSFET umfaßt, und ferner umfassend den Schritt des Aufbringens eines dotierten Polysiliciums auf die Schicht zur Bildung der Gate-Elektrode des MOSFET.
- 35 20. Das Verfahren nach Anspruch 19, bei dem das Polysilicium mit Bor dotiert ist.
- 40 21. Das Verfahren nach Anspruch 19, ferner umfassend den Schritt der Bildung einer dünnen Schicht aus Oxid zwischen der Nitridschicht und der Polysilicium-Gate-Elektrode.
- 45 22. Das Verfahren nach Anspruch 3, bei dem das Anlassen in Gegenwart von Sauerstoff ausgeführt wird.

30

Revendications

- 35 1. Procédé pour la préparation d'un film mince de nitride de silicium ou d'une autre composition contenant de l'azote sur un substrat en silicium, dans une chambre de dépôt par plasma à électrodes parallèles couplée de façon capacitive comprenant les étapes consistant à :
 - disposer une surface du substrat en silicium en contact avec une première électrode d'une paire d'électrodes en plaque, ladite première électrode étant espacée et en regard d'une deuxième électrode en plaque de ladite paire d'électrodes qui est en regard de la surface opposée dudit substrat et à une surface supérieure à ladite première électrode de ladite paire d'électrodes;
 - 40 créer un vide dans une chambre dans laquelle lesdites électrodes et le substrat sont disposés;
 - introduire un gaz réactif contenant de l'azote et ne comprenant pas de composés de silicium dans l'espace situé entre ladite paire d'électrodes; et
 - 45 appliquer une tension alternative ayant une fréquence d'environ 10 KHz ou plus entre lesdites électrodes pour ainsi ioniser et activer le gaz réactif et accélérer ses ions dans le substrat tout en refroidissant ladite première électrode de ladite paire d'électrodes pour empêcher le chauffage dudit substrat, la température dudit substrat étant inférieure à 200°C.
- 50 2. Procédé selon la revendication 1 dans lequel ledit gaz réactif comprend de l'azote pur, de l'ammoniac ou un mélange d'azote et d'hydrogène.
- 55 3. Procédé selon la revendication 1-compris en outre l'étape de recuire le film mince de nitride formé sur ledit substrat.
4. Procédé selon la revendication 3 dans lequel ladite étape de recuit est réalisée en présence d'un gaz non-oxydant.
5. Procédé selon la revendication 1 dans lequel la surface de l'autre électrode de ladite paire d'électrodes est au moins deux fois plus grande que la surface de ladite première électrode.

6. Procédé selon l'une des revendications précédentes pour isoler des régions actives les unes des autres dans un circuit intégré, comprenant les étapes consistant à :
 enlever des parties sélectionnées dudit film de sorte que les parties restantes du film correspondent à des surfaces dans lesquelles des dispositifs actifs doivent être formés dans la plaquette; et
 oxyder les surfaces sur ladite surface de la plaquette qui ne sont pas couvertes par les parties restantes du film de nitrure.

7. Procédé selon la revendication 6 dans lequel le signal de tension alternative a une densité de puissance comprise dans la gamme d'environ 1,6 à 3,2 W/cm² du substrat.

8. Procédé selon la revendication 6 dans lequel le nitrure a une épaisseur qui n'est pas supérieure à 20 nm (200 angströms).

9. Procédé selon la revendication 8 dans lequel ledit film a une épaisseur comprise dans la gamme d'environ 5 à environ 10 nm (50 à environ 100 angströms).

10. Procédé selon la revendication 8 dans lequel le rapport entre l'azote et l'azote plus l'oxygène dans ledit film est d'au moins 90%.

11. Procédé selon la revendication 6 dans lequel la pression dudit plasma est d'environ 10⁻² Torr.

12. Procédé selon la revendication 6 dans lequel ladite surface opposée du substrat comprend une tranchée et ledit film de nitrure reste dans la tranchée après ladite étape d'élimination sélective.

13. Procédé selon l'une des revendications 1 à 5 pour isoler de façon diélectrique des régions actives les unes des autres dans un circuit intégré, comprenant les étapes consistant à :
 former une tranchée dans la surface exposée dudit substrat pour définir une limite d'au moins une zone dans laquelle un dispositif actif doit être disposé; et après que le film de nitrure a été formé sur ladite surface du substrat et le long des parois de ladite tranchée :
 remplir le reste de ladite tranchée avec un matériau isolant.

14. Procédé selon la revendication 13 dans lequel ledit film a une épaisseur d'environ 5 à environ 7 nm (50 à environ 70 angströms).

15. Procédé selon la revendication 13 dans lequel ledit signal de tension alternative a une densité de puissance comprise dans la gamme d'environ 1,6 à environ 3,2 W/cm² sur le substrat.

16. Procédé selon la revendication 13 dans lequel le rapport d'azote à l'azote plus l'oxygène dans ledit film est d'au moins de 90%.

17. Procédé selon les revendications 1, 2 et 3 dans lequel ledit signal de tension alternative à une densité de puissance d'environ 0,4 à environ 2,0 W/cm² du substrat.

18. Procédé selon la revendication 17 comprenant en outre l'étape consistant à déposer une électrode sur la surface dudit film de nitrure qui est opposée au silicium pour former ainsi un condensateur.

19. Procédé selon la revendication 18 dans lequel ledit film de nitrure comprend un diélectrique de grille pour un MOSFET, et comprend en outre l'étape consistant à déposer un polysilicium dopé sur ledit film pour former l'électrode de grille du MOSFET.

20. Procédé selon la revendication 19 dans lequel ledit polysilicium est dopé avec du bore.

21. Procédé selon la revendication 19 comprenant en outre l'étape consistant à former une couche mince d'oxyde entre ledit film de nitrure et ladite électrode de grille en polysilicium.

22. Procédé selon la revendication 3 dans lequel le recuit est réalisé en présence d'oxygène.

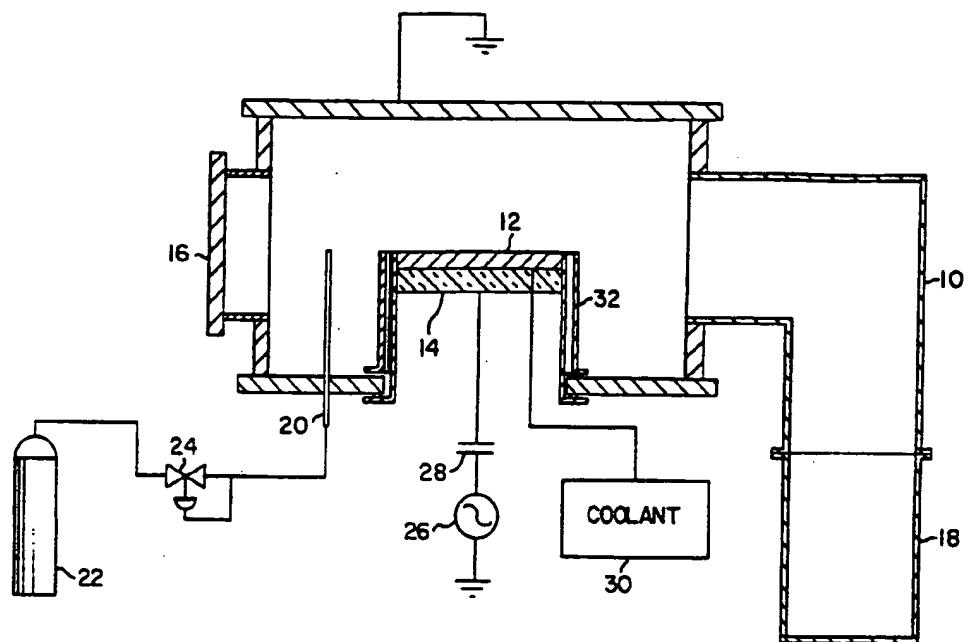


FIG. I

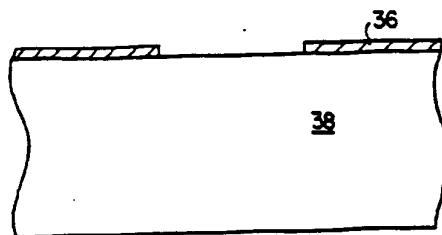


FIG. 2

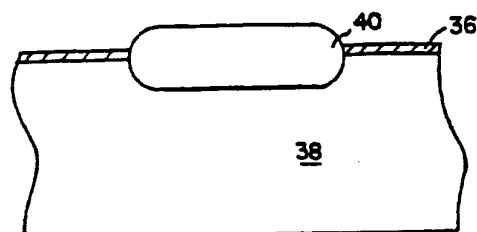


FIG. 3

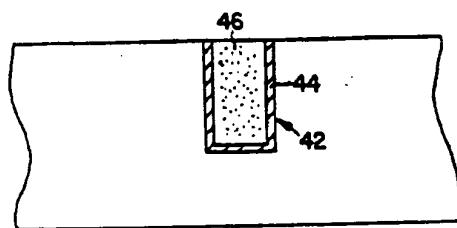


FIG. 4

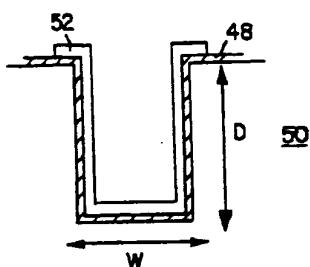


FIG. 5

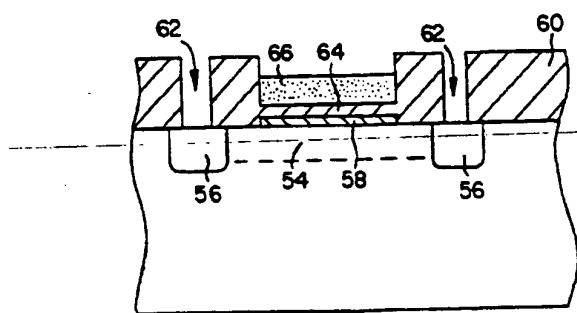


FIG. 6

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